Volume 3
Number 10
September 29, 1964

Inorganic Chemistry

CONTRIBUTION FROM THE NOYES LABORATORY OF CHEMISTRY,
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Preparation and Thermal Stability of Azo and Azomethine Coordination Polyesters[1]

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Received May 4, 1964

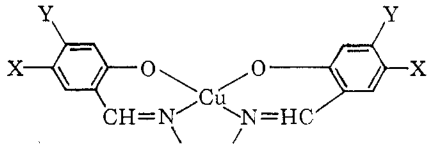
Polyesters of azo and azomethine inner complex bisphenols have been synthesized by interfacial polycondensation with organic diacid chlorides. The low molecular weights of the products obtained with sebacyl chloride and phosgene indicate that the success of the interfacial method is strongly dependent upon the rate of hydrolysis of the diacid chloride. The solubility properties and thermal stabilities of these polyesters are discussed in terms of their structural differences. For the azomethine derivatives an apparent correlation between substituent effects and thermal stability was noted.

A number of inner complexes have been prepared which combine solubility in organic solvents with outstanding thermal and hydrolytic stability.[3] Yet, in spite of the continuing need for new polymer types and for modification of existing polymers, few attempts have been made to employ inner complexes as monomers or comonomers in condensation polymerization reactions. Moreover, most of these attempts have been restricted to the use of melt polymerization procedures and almost invariably have led to materials of low molecular weight.

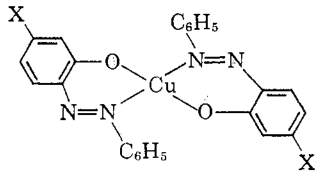
Polyesters containing metal chelate units have been synthesized by fusion of an inner complex diol with phthalic anhydride,[4] by ester exchange between an inner complex diol and an organic ester,[4] and, conversely, by exchange between inner complex esters and organic diols.[5] More recently, substituted beryllium acetylacetonates were employed to yield polyesters, polyamides, polyurethanes, polyalkoxysilanes, and polysilizanes by reaction with the appropriate difunctional reagent in both solution and melt systems.[6]

We now report that conventional interfacial polymerization procedures can be applied to yield polyesters from inner complex bisphenols and organic diacid chlorides.

The complexes bis(2,4-dihydroxybenzaldehyde)ethylenediiminecopper(II) (Ib), bis(2,5-dihydroxybenzaldehyde)ethylenediiminecopper(II) (Ic), and bis(4-phenylazoresorcinol)copper(II) (IIa) were prepared by established procedures and combined with diacid chloride in a two-phase system consisting of aqueous alkali and halogenated hydrocarbon.



Ia, $X = Y = H$
Ib, $X = H, Y = OH$
Ic, $X = OH, Y = H$
Id, $X = H, Y = O\overset{O}{\overset{\|}{C}}C_6H_5$
Ie, $X = O\overset{O}{\overset{\|}{C}}C_6H_5, Y = H$



IIa, $X = OH$
IIb, $X = O\overset{O}{\overset{\|}{C}}C_6H_5$

The solid polymers, isolated by pouring the reaction mixture into acetone, after washing with water and extracting with organic solvents, were generally obtained as infusible and relatively insoluble brown to black powders. Both homopolymers and a copolymer were prepared in this manner using the *m*- and *p*-phthaloyl

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[1] Abstracted from a thesis submitted by Leonard V. Interrante to the University of Illinois in partial fulfillment for the degree of Doctor of Philosophy, 1963.

[2] To whom correspondence should be directed.

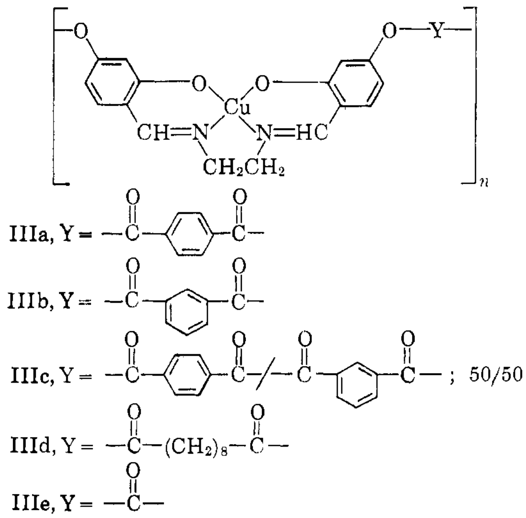
[3] H. Diehl, *Chem. Rev.*, **21**, 40 (1937).

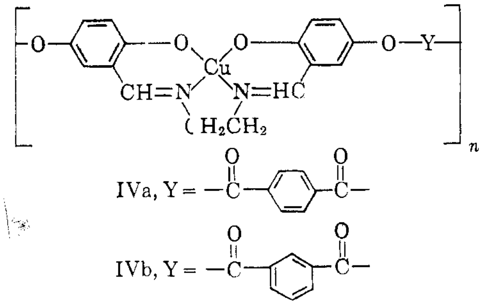
[4] J. C. Bailar, Jr., K. V. Martin, M. L. Judd, and J. McLean, WADC Technical Report 57-391, Part II (1958).

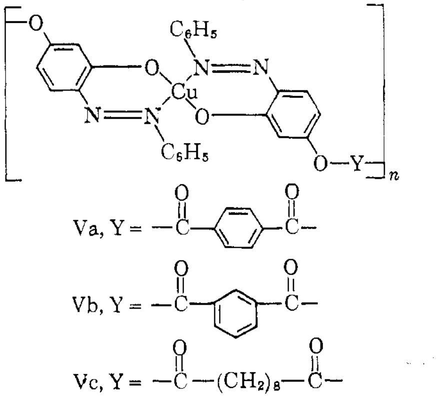
[5] T. R. Patterson, F. J. Pavlik, A. A. Baldoni, and R. L. Frank, *J. Am. Chem. Soc.*, **81**, 4213 (1959).

[6] R. M. Klein and J. C. Bailar, Jr., *Inorg. Chem.*, **2**, 1190 (1963).

chlorides, sebacyl chloride, and phosgene (structures III, IV, and V).







Several attempts were made to carry out some of the same reactions with the azomethine complexes in anhydrous pyridine solution. Although in some cases polymeric products were obtained, all of these attempts resulted in partial or complete decomposition of the metal chelate. The lability of the monomeric complexes in pyridine solution with respect to exchange of the amine residue and the metal ion has been noted in several previous investigations[7-9] and may explain the difficulties encountered with the preparations carried out in this medium.

Evidence for polymer formation was provided by elemental analysis and infrared spectra. The data are summarized in Tables I, II, and III.

The analytical values obtained for the phthalate polyesters, for the most part, are in agreement with the values calculated for the infinite polymer. In addition, the infrared spectra exhibit strong absorption bands at approximately 1730 cm.$^{-1}$, close to the carbonyl stretching frequencies observed for the dibenzoyl esters of the monomeric complexes, and show little evidence of hydroxyl end group absorption.[10]

The low per cent carbon found in the polyesters of complex Ic was also noted in several preparations of the monomeric complex and may be due to partial air oxidation of the coordinated ligand in the course of the polymerization reaction.

The phthalate polyesters were insoluble in most of the common organic solvents and were saponified at room temperature by dilute aqueous alkali. However, whereas the azo derivatives exhibited some solubility in pyridine, dimethylformamide (DMF), and dimethyl sulfoxide (DMSO), the azomethine compounds were virtually insoluble. This difference is reflected in the relative solubilities of the corresponding monomeric complexes and demonstrates the dominant role played by the chelate group in determining the solubility of the coordination polymers. The structural variations among the isomeric azomethine homopolymers and copolymers appeared to have little influence upon their relative solubilities.

The sebacate polyesters, prepared from complexes Ib and IIa, were appreciably more soluble than any of the phthalate derivatives, dissolving completely in pyridine, DMF, and DMSO, and to a lesser extent in tetrahydrofuran, ethanol, and acetone. However, molecular weight determinations (Table I) carried out in these cases, as well as the analytical data and infrared spectra, indicate that the average degree of polymerization is not more than two or three. Therefore, the solubility difference observed may depend more upon a change in the average molecular weight of the polymer than in the nature of the group linking the chelate nuclei.

The attempt to prepare a polycarbonate by interfacial polycondensation also met with only limited success. This procedure, tried only for complex Ib, yielded a product the infrared spectrum of which shows a weak band at 1762 cm.$^{-1}$, close to the expected value for the carbonyl stretching frequency of aryl carbonates.[11] However, the very low intensity of this band and the result of prolonged extraction of the product with acetone indicate that the average degree of polymerization in this case is less than one. Extraction for 5 days removed a material identified as the unchanged monomeric complex in an amount representing approximately 70% of the original product. A corresponding increase in the intensity of the carbonyl stretching frequency was observed in the infrared spectrum of the remaining solid.

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(7) P. Pfeiffer, H. Thielert, and H. Glaser, *J. prakt. Chem.*, **152**, 145 (1939).

(8) P. Pfeiffer and H. Glaser, *ibid.*, **153**, 265 (1939).

(9) R. B. Duffield and M. Calvin, *J. Am. Chem. Soc.*, **68**, 557 (1946).

(10) The extent of the background radiation in this region of the spectrum (4000 to 2000 cm.$^{-1}$) due to light scattering, coupled with the low intensity and wide band width of the hydroxyl stretching absorption of the monomeric complex, prohibits more than a very qualitative indication of the degree of polymerization.

(11) L. J. Bellamy, "The Infrared Spectra of Complex Molecules," John Wiley and Sons, New York, N. Y., 1958, p. 127.

TABLE I

ANALYTICAL DATA FOR AZO AND AZOMETHINE DERIVATIVES

Compd.	Yield, %	% C Calcd.[a]	% C Found	% H Calcd.[a]	% H Found	% N Calcd.[a]	% N Found	Mol. wt. Calcd.	Mol. wt. Found
Ib	84.5	53.1	53.27	3.87	3.91	7.75	7.69		
IIIa	73.5	58.6	58.72	3.29	3.46	5.69	5.81		
IIIb	78.0	58.6	57.84	3.29	3.38	5.69	5.46		
IIIc	82.8	58.6	58.07	3.29	3.45	5.69	5.46		
IIId	37.0	57.6[b]	56.52	4.98[b]	5.14	5.92[b]	5.79	1418[b]	1035[c]
IIIe	25.8	52.6	51.95	3.12	3.62	7.23	6.93		
Ic	78.3	53.1	53.39	3.87	3.91	7.75	7.79		
IVa	83.0	58.6	56.66	3.29	3.32	5.69	5.97		
IVb	84.9	58.6	56.91	3.29	3.32	5.69	6.04		
IIa	53.5	58.8	59.09	3.69	3.94	11.43	11.37		
Va	80.6	62.0	62.74	3.26	3.41	9.03	9.15		
Vb	88.0	62.0	61.94	3.26	3.33	9.03	9.17		
Vc	2.9	60.6[d]	60.58	5.09[d]	4.69	8.31[d]	8.55	674.1[d]	771[e]

[a] Calculated for the monomeric complex or infinite polymer, except as indicated below. [b] Calculated for species containing three chelate and two sebacate units. [c] Determined in pyridine solution by vapor pressure lowering. [d] Calculated for a degree of polymerization of one. [e] Determined in chloroform solution by vapor pressure lowering.

TABLE II

INFRARED DATA FOR AZOMETHINE COMPLEXES[a,b]

Compd.	Absorption bands in the region 1400–4000 cm.$^{-1}$, tentative assignments[c] O—H stretch	C—H stretch	C=O stretch	C=N stretch	Aromatic ring vibrations I	II	III
Ib	3260 w	2915 vw	. . .	1615 s		1540 m	1452 m
Id	. . .	2915 vw, 2860 vw, sh	1730 s	1630 s	1608 s	1538 m	1444 m, 1432
IIIa	. . .	2910 vw	1730 s	1625 s	1605 s	1532 m	1445 m, 1430 m
IIIb	. . .	2900 vw	1732 s	1615 s, br		1530 s	1443 s, 1429 s
IIIc	. . .	2900 vw	1730 s	1626 s	1603 s	1528 m	1443 m, 1430 m
IIId	3300 vw	2920 w	1748 m	1615 s		1536 m	1444 m
IIIe	Not detd.	2910 vw (KBr)	1762 w	1617 s		1532 m	1444 m
Ic	3250 m, br	2915 vw	. . .	1630 s		1545 s	1467 s, 1447 s
Ie	. . .	3050 vw	1725 s	1632 s		1537 s	1463 s, 1453 w, sh, 1436 m
IVa	. . .	2910 vw	1723 s	1623 s, br		1532 s, br	1445 s, br
IVb	. . .	2910 vw	1720 s	1610 s, br		1523 s, br	1455 s, 1430 s

[a] O–H and C–H absorptions determined using hexachlorobutadiene mulls, unless otherwise indicated; others determined using KBr disk technique. [b] vs, very weak; w, weak; m, medium; s, strong; br, broad; sh, shoulder. [c] Reference: L. J. Bellamy, "The Infrared Spectra of Complex Molecules," 2nd Ed., John Wiley and Sons, Inc., New York, N. Y., 1958, pp. 64, 95, 178, 263.

TABLE III

INFRARED DATA FOR DERIVATIVES OF BIS(4-PHENYLAZORESORCINOL)COPPER(II)[a,b]

Compd.	Absorption bands in the region 1400–4000 cm.$^{-1}$, tentative assignments[c] O—H stretch	C—H stretch	C=O stretch	Aromatic ring vibrations I	II	III
IIa	3340 m, br	3080 vw	. . .	1603 s	1540 m	1467 s, 1457 s
IIb	. . .	3075 vw	1738 s	1606 s	1536 m	1470 s, 1455 s
Va	. . .	3065 vw	1733 s	1601 s	1531 m	1465 m, 1453 m
Vb	. . .	3070 vw	1740 s	1606 s	1538 m	1470 s, 1457 s
Vc	. . .	3080 vw, 2925 w, 2850 vw	1756 s	1603 s	1530 m	1468 s, 1453 s

[a] O–H and C–H absorption frequencies determined using hexachlorobutadiene mulls, others determined using KBr disk technique. [b] vw, very weak; w, weak; m, medium; s, strong. [c] Reference: L. J. Bellamy, "The Infrared Spectra of Complex Molecules," 2nd Ed., John Wiley and Sons, Inc., New York, N. Y., 1958, pp. 64, 95, 178, 271.

Furthermore, it was discovered that an increase in the relative proportion of alkali over that required to neutralize the complex bisphenol decreased the proportion of carbonate in the product.

These results indicate that the interfacial method, as applied to reactions between the inner complex bisphenols and the diacid chlorides sebacyl chloride and phosgene, leads to a considerable loss of acid chloride

TABLE IV

THERMAL STABILITY DATA FOR AZOMETHINE COMPLEXES[a]

Compd.	% dec. after successive 12-hr. periods at 200°	250°	300°	Post-heating infrared spectra[b]
Ia	0.0	10.7	27.3	(1)
Ib	1.3	5.2	8.7	(5)
Ic[c]	0.6	3.2	18.9	(2)
Id	0.2	1.4	33.5	(2)
Ie[d]	0.4	0.7	40.6	(2)
IIIa	2.6	7.9	23.3	(4)
IIIb	2.6	4.8	23.6	(3)
IIId	4.7	9.7	20.2	(2)
IVa	2.8	5.9	15.7	(4)
IVb[e]	6.9	35.4	60.2	(2)

[a] Measurements conducted under nitrogen, sample weight 200 mg., except as indicated. [b] (1) Spectrum entirely featureless; (2) weak band at approximately 1600 cm.$^{-1}$, otherwise featureless; (3) weak bands at approximately 1715, 1600, and 600–800 cm.$^{-1}$; (4) major absorption bands still observable but shifted to slightly lower frequencies and considerably broadened and weakened; (5) absorption bands broadened but basically unaltered in number and frequency. [c] Average of two determinations, one conducted under argon. [d] Sample weight 90.6 g. [e] Average of two determinations.

TABLE V

THERMAL STABILITY DATA FOR BIS(4-PHENYLAZORESORCINOL)-COPPER(II) AND ITS DERIVATIVES[a]

Compd.	% dec. after successive 12-hr. periods at 200°	250°	300°
IIa	14.1	17.9	20.6
IIb[b]	0.2	33.9	36.3
Va	0.6	18.4	28.8
Vb	1.0	18.9	24.4

[a] Measurements conducted under nitrogen, sample weight 200 mg., except as indicated. [b] Sample weight 68.1 mg.

through hydrolysis. This may be due to a combination of the high rates of hydrolysis of these diacid chlorides[12] and a decreased reactivity of the free phenoxide group of the complex toward esterification. The electronegative substituents on the benzene ring[13] as well as the coordination of these substituents to the central metal ion[14] could well account for such a decrease in reactivity.

Thermal Stability.—The thermal stabilities of each of the monomeric complexes, their dibenzoyl esters, the polymers, and the parent azomethine complex bis-(salicylaldehyde)ethylenediiminecopper(II) (Ia) were determined by measuring the % weight loss over a 12-hr. period at a designated temperature. All measurements were performed under an inert atmosphere (Tables IV and V).

These data are supplemented by post-heating infrared spectra obtained for the azomethine samples after the final measurement at 300°. These spectra provide an independent qualitative comparison of the extent of decomposition as indicated by the degree of broadening, decrease in intensity, and shift in frequency of the absorption bands.

This information has been classified for convenience into five categories, depending upon the extent of change in the spectrum, and is included in Table IV. As indicated in this table, several of the azomethine polymers were found to be fairly stable at 250°, but all were largely decomposed at 300°. Also apparent from a cursory examination of the data is the substantial increase in stability resulting from substitution of a hydroxyl group on the chelate nucleus. Thus, the parent complex, Ia, decomposes to a significant extent even at 250°,[15] whereas the 4-hydroxy derivative Ib is reasonably stable at 300°. This observation is contrary to the results of another study, in which complex Ib and others of this type were reported to be less thermally stable than the complexes of type Ia.[16] However, in this case the measurements were conducted in air rather than in inert atmosphere, which may well have resulted in the oxidative decomposition of complex Ib rather than the thermal decomposition.

The improved thermal stability of the hydroxy-substituted complexes over that of the unsubstituted derivative may be explained by considering the electronic effects induced by this substitution. It is well known that the introduction of electron-donating groups into an aromatic ring in a metal chelate compound often results in an increase in the strength of attachment between ligand and metal ion.[17] This has been attributed to both resonance and inductive effects which increase the electron density on the donor atoms.

If it is assumed that the metal–ligand bond is the principal factor determining the thermal stability of these chelates, this effect may be used to explain both the increased stability of the hydroxy derivatives over the unsubstituted complex and the relative stabilities of complexes Ib, Ic, and their dibenzoyl derivatives and polymers. Thus, in compound Ib the hydroxyl group is *para* to the azomethine group and may contribute electron density to the nitrogen atom by direct resonance interaction.

In the case of compound Ic, resonance forms which transfer electrons directly from the hydroxyl group to the donor atoms cannot be written; however, it seems reasonable that the tendency of the 2-oxygen atom to donate π-electron density to the benzene ring would be diminished by substituent groups, such as the 5-hydroxyl, which increase the charge density at the 2-carbon atom. Therefore, by retaining more enolate character relative to that in the unsubstituted compound, this group should act as a better donor toward the copper ion. Alternatively, one may postulate that the 5-hydroxyl group opposes the resonance of the 2-oxygen atom with the benzene ring by means of a re-

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(12) V. V. Korshak, I. M. Frunze, S. V. Vinogradova, V. V. Kurashev, and A. S. Lebedeva, *Izv. Akad. Nauk SSSR, Otd. Khim. Nauk*, 1807 (1962); *Chem. Abstr.*, **58**, 8872 (1963).

(13) W. M. Eareckson, *J. Polymer Sci.*, **40**, 399 (1959).

(14) M. M. Jones, *J. Tenn. Acad. Sci.*, **38** (3), 87 (1963).

(15) A recent publication [W. W. Wendlandt, S. I. Ali, and C. H. Stembridge, *Anal. Chim. Acta*, **30**, 84 (1964)] reports that this compound begins to lose weight in air at 310°, when the temperature is increased at a rate of 5°/min. Evidence for an induction period of at least 4 hr. preceding the thermal decomposition of chelates of this type in air has previously been obtained[16] and may explain the difference between their data and ours.

(16) C. S. Marvel, S. A. Aspey, and E. A. Dudley, *J. Am. Chem. Soc.*, **78**, 4905 (1956).

(17) A. E. Martell and M. Calvin, "Chemistry of the Metal Chelate Compounds," Prentice-Hall, Inc., Englewood Cliffs, N. J., 1959, p. 171.

pulsion between its lone-pair electrons and the π-electrons of the ring.[18]

Support for these arguments is obtained from measurements of the relative acidities of substituted phenols which indicate an increase in the basicity of the phenoxide ion by *ortho*- or *para*-substitution of hydroxyl and other π-electron donors.[19]

These arguments apply equally well in explaining the relative stabilities of the polymers and dibenzoyl derivatives compared to the monomeric complexes. Substitution of carbonyl for hydrogen of the hydroxyl groups would be expected to decrease the effectiveness of the oxygen atom as an electron donor. This is reflected in the general decrease in thermal stability of the polymers and dibenzoyl esters compared to that of the monomeric complexes. As might be expected, this decrease is much more pronounced for the derivatives of complex Ib (in which direct resonance interaction is possible) than for those of complex Ic.

Among the carbonyl-substituted compounds, an appreciable difference in thermal stability was not generally observed, although the extent of decomposition at 300°, as well as the post-heating spectra, indicate that the simple esters are degraded to a somewhat greater extent than the polyesters.

The thermal instability exhibited by polymer IVb, the isophthalate polyester of complex Ic, was entirely unexpected and does not yield to simple interpretation. However, this result, although repeated in a duplicated determination (Table IV), is subject to some question in the light of the relatively poor analytical data obtained for both the isophthalate and terephthalate polyesters of this complex. The thermal stability may be strongly influenced by the impurities, such as copper oxide, which are likely to be present.

A change in the nature of the linking group from aryl to alkyl, as indicated by both the thermal stability data and post-heating spectrum obtained for the sebacate derivative IIId, appears to result in a decrease in the thermal stability of the polyester. This result implies that, at least in this case, the linking group exerts a more direct effect upon the thermal stability of the chelate polymer than simply influencing the strength of the metal–ligand bonds.

In direct contrast to the azomethine compounds, the azo polyesters, which are all unstable at 250°, were found to be more stable than the monomeric complex from which they are derived. From this observation, it seems probable that the strength of the metal–ligand bond, unlike that of the azomethine derivatives, may not be the principal factor determining the thermal stability of the azo complexes.

It may be significant that one of the main products of the decomposition of the monomeric complex IIa was found to be the free ligand, 4-phenylazoresorcinol, which began to sublime from the heated sample just below 200°. No evidence for sublimation from the carbonyl-substituted azo compounds was found. This may indicate a fundamental difference in the mode of decomposition of these derivatives, depending, in the case of the monomeric complex, upon the availability of the proton on the free phenolic hydroxyl groups to displace copper ion from the ligand.

Among the carbonyl-substituted derivatives of the monomeric complex IIa, the pattern of thermal stability appears to parallel roughly that of the azomethine complexes, exhibiting no major change in stability among the simple ester and the isomeric phthalate polyesters.

Experimental

Preparation of Complexes.—Bis(salicylaldehyde)ethylenediiminecopper(II) (Ia),[20] bis(2,4-dihydroxybenzaldehyde)ethylenediiminecopper(II) (Ib),[21] and bis(4-phenylazoresorcinol)copper(II) (IIa)[22] were prepared and purified according to the directions given in the literature. Bis(2,5-dihydroxybenzaldehyde)ethylenediiminecopper(II) (Ic), although previously synthesized by a different method,[23] was prepared here by the procedure used for complex Ib. In this case, the best results were obtained when the reaction was conducted under nitrogen, for the ligand oxidizes readily.

The azomethine complexes Ib and Ic were rendered anhydrous by drying at 110°, *in vacuo*, and were found to take up water rapidly upon exposure to the atmosphere.

Dibenzoyl Derivatives.—Complexes Ib, Ic, and IIa, in aqueous alkali solution, were treated with benzoyl chloride, and the solid product was recrystallized from chloroform–ether[21] or, in the case of the derivative of complex IIa, from xylene.[22] The new compound, bis(2-hydroxy-5-benzoylbenzaldehyde)ethylenediiminecopper(II) (Ie), was obtained as silky brown crystals, m.p. 294–298°.

Anal. Calcd. for $C_{30}H_{22}N_2O_6Cu$: H, 3.86; Cu, 63.2; N, 4.91. Found: H, 3.88; C, 62.93; N, 5.04.

Preparation of Polymers.—Except for the reaction involving phosgene, all of the interfacial polymerizations were carried out by the procedure described by Eareckson.[13] In this method, the complex (8.33×10^{-3} mole) in aqueous alkali (1.67×10^{-2} mole in 100 ml. of water) and the diacid chloride (8.33×10^{-3} mole) in ether–chloroform, dichloromethane, or *sym*-tetrachloroethane (50 ml.) were mixed with detergent[24] (0.5 g.) in a Waring blender. After mixing for 5–8 min., the solid polymer was isolated by pouring the reaction mixture into acetone. Repeated washings with water and, in several cases, extraction with solvents such as acetone, ethanol, and pyridine served to remove inorganic salts, detergent, and unchanged starting material from the polymeric product. For the preparations employing sebacyl chloride, the degree of polymerization was highest when dichloromethane was used as the organic diluent.

A similar procedure was used for the reaction between complex Ib and phosgene except that phosgene (1.09×10^{-2} mole) was added as a gas to the complex (1.00×10^{-2} mole) in a mixture of aqueous alkali (2.15×10^{-2} mole in 30 ml. of water) and *sym*-tetrachloroethane (17 ml.) in a round-bottom flask. Rapid stirring and the use of a Dry Ice condenser served to minimize loss of phosgene.

Attempts to prepare the azomethine polyesters in pyridine solution (using reagent grade pyridine dried over phosphorus

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(18) J. N. Murrell, *Roy. Inst. Chem.* (London), *Lectures*, 6 (1963) (2); D. T. Clark, J. N. Murrell, and J. M. Tedder, *J. Chem. Soc.*, 1252 (1963).

(19) G. E. K. Branch and M. Calvin, "The Theory of Organic Chemistry," Prentice-Hall, Inc., New York, N. Y., 1944, p. 249; C. A. Streuli, *Anal. Chem.*, **32**, 407 (1960).

(20) P. Pfeiffer and H. Pfitzner, *J. prakt. Chem.*, **145**, 243 (1936).

(21) P. Pfeiffer, E. Breith, E. Lübbe, and T. Tsumaki, *Ann.*, **503**, 84 (1933).

(22) P. Pfeiffer, Th. Hesse, H. Pfitzner, W. Scholl, and H. Thielert, *J. prakt. Chem.*, **149**, 217 (1937).

(23) T. Tanaka, *Bull. Chem. Soc. Japan*, **33**, 259 (1960).

(24) Sodium lauryl sulfate, E. I. du Pont de Nemours and Co.

pentoxide) were unsuccessful. A saturated solution of the complex was treated with an equimolar amount of the gaseous diacid chloride (phosgene) or a solution of the diacid chloride in dry acetone. The solid product was isolated by pouring the reaction mixture into water, followed by washing with water and organic solvents to remove impurities. The elemental analysis and infrared spectra of the products obtained indicated slight polymerization and partial decomposition of the chelate.

Infrared Absorption Spectra.—All infrared spectra were obtained using a Perkin-Elmer Model 21 infrared spectrophotometer with sodium chloride optics. Samples were prepared as potassium bromide disks or hexachlorobutadiene mulls.

To avoid absorption of water, mulls of the azomethine derivatives were prepared in a drybox, after drying the sample at 110°, *in vacuo*.

Thermal Stability Measurements.—Measurements were performed under nitrogen or argon using a simple thermogravimetric balance similar to that described by Winslow and Matreyek.[25] The accuracy of the apparatus was checked using reagent grade $CuSO_4 \cdot 5H_2O$ as a standard. The weight losses observed at two different temperatures (125 and 270°) with a 200-mg. sample of $CuSO_4 \cdot 5H_2O$ heated under nitrogen for consecutive 12-hr. periods agree to within 2% of the expected values at these temperatures.[26]

The weight loss after 12 hr. at 150° was usually slight and presumed to be due to loss of water. The thermal stability data are reported in Tables IV and V as per cent weight loss at the designated temperature relative to the sample weight at 150°, after heating for 12 hr. at that temperature. Temperatures were constant to within ±5° and the weight of sample used was approximately 200 mg., except as noted. The reliability of these data has been checked in two cases by duplicate determinations which agree to within 5% of the given value for weight losses greater than 4%.

Acknowledgments.—The authors wish to thank Mr. J. Nemeth and his associates for analyses and molecular weight measurements, and Mr. D. H. Johnson and staff who provided most of the infrared spectra. We are indebted to the National Science Foundation for financial support, which was extended to Leonard V. Interrante through a fellowship.

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(25) F. H. Winslow and W. Matreyek, *J. Polymer Sci.*, **22**, 315 (1956).

(26) W. W. Wendlandt, *Anal. Chim. Acta*, **27**, 313 (1962).

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Reactions of Triethylamine with Copper Halides. II. Internal Oxidation–Reduction of Dichlorobis(triethylamine)copper(II)[1,2]

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Received May 11, 1964

Triethylamine and copper(II) chloride react at −45° to form the crystalline complex $CuCl_2 \cdot 2N(C_2H_5)_3$, characterized by composition and by its electronic and e.p.r. spectra. Upon warming to about 0° this complex undergoes internal electron transfer to give a diamagnetic solid. The hydrolysis products of diethylvinylamine are obtained from this diamagnetic product. A relation to the enzymic copper-catalyzed oxidative dealkylation of amines is suggested. Further warming of the anhydrous reaction mixture causes reappearance of the e.p.r. signal of Cu(II). A change in the coordination environment is indicated by a shift in the anisotropic g values from those of the original complex. The transient paramagnetic species react further to give the diamagnetic final product previously observed[1] in the direct reaction of triethylamine with copper(II) chloride at elevated temperatures. Some n.m.r. data offer additional evidence corroborating the previous suggestion[1] on the nature of the final product.

Introduction

In the previous work,[1] it was shown that an irreversible oxidation–reduction reaction is easily induced on warming a mixture of anhydrous copper(II) chloride and an excess of triethylamine. Pressure–composition phase studies and hydrolysis studies showed that the reaction corresponds to the equations

$$CuCl_2(c) + 2(C_2H_5)_3N(l) \longrightarrow A(\text{dark solid}) \qquad (1)$$

$$A \underset{25^\circ}{\overset{6\text{ mm.}}{\rightleftharpoons}} B(\text{dark liquid}) + (C_2H_5)_3N(g) \qquad (2)$$

$$B \xrightarrow[(\text{NaOH})]{H_2O} CuCl + (NaCl) + \sim 0.85(C_2H_5)_3N + C(\text{tar}) \qquad (3)$$

The recovery of a total of *ca.* 1.85 moles of the original 2.00 moles of triethylamine bound in the reaction mixture suggests that the dark tarry product C is a polymeric amine derived from the oxidation of *ca.* $^1/_6$ mole of triethylamine. To account for the reduction of 1 mole of copper(II) to copper(I), repeated steps of oxidative deprotonation of triethylamine were postulated.

Using the pure components, the equilibrium reaction

$$(C_2H_5)_3NHCl(s) + CuCl \cdot N(C_2H_5)_3(s) \underset{25^\circ}{\overset{6\text{ mm.}}{\rightleftharpoons}} (C_2H_5)_3NHCuCl_2(\text{oil}) + (C_2H_5)_3N(g) \qquad (4)$$

was observed. Both the pressure–composition behavior and the phase changes suggest a close relation between this system and the products A and B above.

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(1) Paper I: J. T. Yoke, J. F. Weiss, and G. Tollin, *Inorg. Chem.*, **2**, 1210 (1963).

(2) This investigation was supported by P.H.S. grant GM from 11511-01 the National Institutes of Health, Public Health Service.

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